CATALYST AND PROCESS FOR THE OXIDATION OF ETHANE AND/OR ETHYLENE

The present invention relates to a catalyst for the oxidation of ethane and/or ethylene to acetic acid and to a process for the production of acetic acid utilising the aforesaid catalyst.

Catalysts and processes for the production of acetic acid by the oxidation of ethane and ethylene are known in the art from, for example, US-A-4,250,346; EP-A-0407091; DE-A-19620542; and DE-A-19630832.

US Patent No. 4,250,346 discloses the oxidative dehydrogenation of ethane to ethylene in a gas phase reaction at relatively high levels of conversion, selectivity and productivity at a temperature less than 500°C using as catalyst a composition comprising the elements molybdenum, X and Y in the ratio

$$Mo_aX_bY_c$$

wherein

X is Cr, Mn, Nb, Ta, Ti, V and/or W, and preferably Mn, Nb, V and/or W

Y is Bi, Ce, Co, Cu, Fe, K, Mg, Ni, P, Pb, Sb, Si, Sn, Tl and/or U, and preferably Sb, Ce and/or U,

a is 1,

b is 0.05 to 1.0 and

c is 0 to 2, and preferably 0.05 to 1.0, with the proviso that the total value of c for Co, Ni and/or Fe is less than 0.5.

EP-A-0407091 discloses a process for the production from gaseous ethane and/or ethylene of a product comprising ethylene and/or acetic acid, by contacting the ethane and/or ethylene and a molecular oxygen-containing gas at elevated temperature with a calcined molybdenum-containing ethane oxidative dehydrogenation catalyst composition characterised in that molybdenum in the oxidative dehydrogenation catalyst composition is replaced in

whole or in part by either rhenium or a combination of rhenium and tungsten.

Also disclosed in EP-A-0407091 is a catalyst comprising the elements A, X and Y in combination with oxygen, the gram-atom ratios of the elements A:X:Y being a:b:c,

wherein A = $Mo_dRe_eW_f$,

X = Cr, Mn, Nb, Ta, Ti, V and/or W, and preferably Mn, Nb, V and/or W,

Y = Bi, Ce, Co, Cu, Fe, K, Mg, Ni, P, Pb, Sb, Si, Sn, Tl and/or U, and preferably Sb, Ce and/or U,

a = 1,

b = 0 to 2, preferably 0.05 to 1.0,

c = 0 to 2, preferably 0.001 to 1.0, and more preferably 0.05 to 1.0 with the proviso that the total value of c for Co, Ni, and/or Fe is less than 0.5,

d + e + f = a,

d is either zero or greater than zero,

e is greater than zero, and

f is either zero or greater than zero.

DE-A-19620542 discloses a catalyst for the selective oxidation of ethane and/or ethylene to acetic acid containing the elements Mo, Pd, Re, X and Y in the gram atom ratios a:b:c:d:e in combination with oxygen

$$Mo_aPd_bRe_cX_dY_e \qquad (I)$$

where the symbols X, Y have the following signification:

X = Cr, Mn, Nb, B, Ta, Ti, V and/or W

Y = Bi, Ce, Co, Cu, Te, Fe, Li, K, Na, Rb, Be, Mg, Ca, Sr, Ba, Ni, P, Pb, Sb, Si, Sn, Tl and/or U;

the indices a, b, c, d and e stand for the gram atom ratios of the corresponding elements, where a = 1, b>0, c>0, d = 0.05 to 2 and e = 0 to 3. Also disclosed in DE-A-19620542 is a process for the selective production of acetic acid from a gaseous charge of ethane, ethylene or mixtures thereof in addition to oxygen by bringing the gaseous charge into contact with a catalyst of the formula (I).

Finally, DE-A-19630832 discloses a catalyst for the selective oxidation of ethane, ethylene or mixtures thereof as well as oxygen, containing the elements Mo, Pd, X and Y in the gram ratios a:b:c:d in combination with oxygen

$$Mo_aPd_bX_cY_d \qquad (I)$$

where the symbols X, Y have the following signification:

X stands for one or more of the elements selected from the group Cr, Mn, Nb, Ta, Ti, V and W;

Y stands for one or more of the elements selected from the group B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Ir, Cu, Ag, Au, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl, and U;

the indices a, b, c, d stand for the gram atom ratios of the corresponding elements, where

a = 1; b>0; c>0 and d = 0-2. Also disclosed in DE-A-19630832 is a process for the selective production of acetic acid from a gaseous charge of ethane, ethylene or mixtures thereof in addition to oxygen by contacting the gaseous charge with a catalyst of the formula (I).

International patent publication WO 98/47850 published after the priority date of the present application relates to a process and catalyst for preparing acetic acid by catalytic oxidation of ethane. The catalyst used has the formula $W_aX_bY_cZ_d$ in which X stand for one or more elements selected from the group Pd, Pt, Ag and/or Au; Y stands for one or more elements selected from the group V, Nb, Cr, Mn, Fe, Sn, Sb, Cu, Zn, U, Ni and/or Bi; Z stands for one or more elements selected from the group Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Ru, Os, Co, Rh, Ir, B, Al, Ga, In, Tl, Si, Ge, Pb, P, As and/or Te in the formula a=1, b is greater than 0, c is greater than 0 and d is a number from 0 to 2. Tungsten is thus an essential component of the catalyst.

US 5750777 (equivalent to EP-A-719756) relates to production of acetic acid by oxidation of ethane in the presence of a catalyst in which the active phase comprises vanadium, titanium, molybdenum, phosphorus and oxygen which includes a dopant from the following elements : K, Rb, Cs, Ca, Mg, Zr, Hf, Nb, Ta, Cr, W, Mn, Re, Fe, Ru, Os, Rh, Ir, Ni, Pd, Cu, Ag, Zn, Cd, Tl, Si, Ge, Sn, As, Sb, Bi, Ga and the rare earths. However, there are no specific examples containing silver or iridium.

US patent US 4,568,790 relates to a process for the low temperature catalytic oxydehydrogenation of ethane to ethylene in a gas phase using a catalyst having a calcined composition of $Mo_aV_bNb_cSb_d$ wherein a = 0.5 to 0.9, b = 0.1 to 0.4, c = 0.001 to 0.2 and d = 0.001 to 0.1.

US patent US 4,596,787 relates to a process for preparing a supported

catalyst for the low temperature oxydehydrogenation of ethane to ethylene in a gas phase, including catalysts having a calcined composition containing $Mo_aV_bNb_cSb_dX_e$ wherein X = nothing or at least one of the following : Li, Sc, Na, Be, Mg, Ca, Sr, Ba, Ti, Zr, Hf, Y, Ta, Cr, Fe, Co, Ni, Ce, La, Zn, Cd, Hg, Al, Tl, Pb, As, Bi, Te, U, Mn and W, a = 0.5 to 0.9, b = 0.1 to 0.4, c = 0.001 to 0.2, d = 0.001 to 0.1 and e = 0.001 to 1.0 for X equal to at least one element and e = 0 for X =0.

There remains a need for a catalyst for the selective oxidation of ethane and/or ethylene to acetic acid and a process for the selective production of acetic acid employing the catalyst. We have found that oxidation catalysts employing silver and/or iridium as an essential component can fulfil the need for a selective oxidation catalyst and process employing same.

Accordingly, the present invention provides a catalyst composition for the selective oxidation of ethane and/or ethylene to acetic acid which composition comprises in combination with oxygen the elements:-

$$Mo_a.W_b.Ag_c.Ir_d.X_e.Y_f \qquad (I)$$

wherein X is the elements Nb and V;

Y is one or more elements selected from the group consisting of :

Cr, Mn, Ta, Ti, B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Cu, Au, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl, U, Re and Pd;

a, b, c, d, e and f represent the gram atom ratios of the elements such that

$0 < a \leq 1$, $0 \leq b < 1$ and $a + b = 1$;

$0 < (c + d) \leq 0.1$;

$0 < e \leq 2$; and

$0 \leq f \leq 2$.

Catalysts embraced within the formula (I) include:-

$Mo_a.W_b.Ag_c.X_e\ Y_f$

$Mo_a.W_b.Ir_d.X_e\ Y_f$

$Mo_a.W_b.[Ag+Ir]_{c+d}.X_e.Y_f$

$Mo_a.Ag_c.X_e.Y_f$

$Mo_a.Ir_d.X_e.Y_f$

$Mo_a.[Ag+Ir]_{c+d}.X_e.Y_f$

$[Mo+W]_{a+b}.Ag_c.X_e.Y_f$

$[Mo+W]_{a+b}.Ir_d.X_e.Y_f$

$$[Mo+W]_{a+b}.[Ag+Ir]_{c+d}.X_e.Y_f$$

Examples of suitable catalysts having the formula (I) include:-

(i) $Mo_{0.37}.Ag_{0.01}.Re_{0.25}.V_{0.26}.Nb_{0.07}.Sb_{0.03}.Ca_{0.02}.Oy'$ which renormalised on the basis of Mo is the same as $Mo_{1.00}.Re_{0.69}.V_{0.72}.Nb_{0.25}..Sb_{0.08}.Ca_{0.03}.Ag_{0.028}Oy$;

(ii) $Mo_{0.37}.Ir_{0.01}.Re_{0.25}.V_{0.26}.Nb_{0.07}.Sb_{0.03}.Ca_{0.02}.Oy'$ which renormalised on the basis of Mo is the same as $Mo_{1.00}.Re_{0.69}.V_{0.72}.Nb_{0.25}..Sb_{0.08}.Ca_{0.03}.Ir_{0.028}Oy$;

(iii) $Mo_{1.00}.V_{0.25}.Nb_{0.12}..Ag_{0.014}Oy$; and

(iv) $Mo_{1.00}.V_{0.25}.Nb_{0.12}..Ag_{0.000028}.Ir_{0.0000018}Oy$.

wherein y' and y are numbers which satisfy the valencies of the elements in the composition for oxygen.

An advantage of catalyst compositions according to the present invention is that they can be more active and selective in converting ethane and/or ethylene to acetic acid.

Preferably, silver and/or iridium is present in an effective amount such that c + d is at least 10^{-6}. Preferably, c and d are such that $(c+d) \leq 0.05$. Silver is more effective than iridium. Preferably, more silver is present than iridium on a gram atom basis. Preferably, c and d are such that c is at least 10 times greater than d.

Preferably, e is at least 0.05, more preferably e is at least 0.2. Preferably, e is no greater than 0.5. Yet more preferably, e is such that $0.05 \leq e \leq 0.5$. Still more preferably, e is such that $0.2 \leq e \leq 0.5$.

Preferably, f is at least 10^{-6}. Preferably, f is no greater than 0.2. Yet more preferably, f is such that $10^{-6} \leq f \leq 0.2$.

Preferably, Y is at least one element selected from the group consisting of Cu, Pd, Pt, Re, Ru and Sb.

Preferably, a is at least 0.1. More preferably, a is at least 0.5. Preferably, b is no greater than 0.9.

The catalyst compositions may be prepared by any of the methods conventionally employed for the preparation of catalysts. Suitably the catalyst may be prepared from a solution of soluble compounds and/or complexes and/or compounds of each of the metals. The solution is preferably an aqueous system having a pH in the range from 1 to 12, preferably from 2 to 8, at a temperature of from 20° to 100°C.

Generally, a mixture of compounds containing the elements is prepared by dissolving sufficient quantities of soluble compounds and dispersing any insoluble compounds so as to provide a desired gram-atom ratio of the elements in the

catalyst composition. The catalyst composition may then be prepared by removing the solvent from the mixture. The catalyst may be calcined by heating to a temperature of from 200 to 550°C, suitably in air or oxygen, for a period of from 1 minute to 24 hours. Preferably, the air or oxygen is slowly flowing.

The catalyst may be used unsupported or supported. Suitable supports include silica, alumina, zirconia, titania, silicon carbide and mixtures of two or more thereof.

Further details of a suitable method for preparing a catalyst composition may be found in, for example, EP-A-0166438.

The catalyst may be used in the form of a fixed or a fluidised bed.

In another embodiment the present invention provides a process for the production of acetic acid from a gaseous mixture comprising ethane and/or ethylene which process comprises contacting the gaseous mixture with a molecular oxygen-containing gas at elevated temperature in the presence of a catalyst composition as hereinbefore described.

The feed gas comprises ethane and/or ethylene, preferably ethane.

Ethane and/or ethylene may be used in substantially pure form or admixed with one or more of nitrogen, methane, carbon dioxide and water in the form of steam, which may be present in major amounts, for example greater than 5 volume percent or one or more of hydrogen, carbon monoxide, C_3/C_4 alkenes and alkenes, which may be present in minor amounts, for example less than 5 volume percent.

The molecular oxygen-containing gas may be air or a gas richer or poorer in molecular oxygen than air, for example oxygen. A suitable gas may be, for example, oxygen diluted with a suitable diluent, for example nitrogen.

It is preferred to feed, in addition to ethane and/or ethylene and the molecular oxygen-containing gas, water (steam) because this can improve the selectivity to acetic acid.

The elevated temperature may suitably be in the range from 200 to 500°C, preferably from 200 to 400°C.

The pressure may suitably be atmospheric or superatmospheric, for example in the range from 1 to 50 bar, preferably from 1 to 30 bar.

The catalyst composition is preferably calcined before use in the process of the invention. Calcination may suitably be achieved by heating at a temperature suitably in the range from 250 to 500°C in the presence of an oxygen-containing gas, for example air.

Operating conditions and other information applicable to the performance of the invention may be found in the aforesaid prior art, for example US Patent No. 4,250,346.

In a preferred embodiment, the oxidation catalyst of the present invention may be used in an integrated process for the production of acetic acid and/or vinyl acetate such as that described, for example, in International patent publication WO 98/05620, the contents of which are incorporated herein by reference. Thus, according to this embodiment, there is provided an integrated process for the production of acetic acid and/or vinyl acetate which comprises the steps :

(a) contacting in a first reaction zone a gaseous feedstock comprising ethylene and/or ethane and optionally steam with a molecular oxygen-containing gas in the presence of a catalyst active for the oxidation of ethylene to acetic acid and/or ethane to acetic acid and ethylene as hereinbefore described, to produce a first product stream comprising acetic acid, water and ethylene (either as unreacted ethylene and/or as co-produced ethylene) and optionally also ethane, carbon monoxide, carbon dioxide and/or nitrogen; and

(b) contacting in a second reaction zone in the presence or absence of additional ethylene and/or acetic acid at least a portion of the first gaseous product stream comprising at least acetic acid and ethylene and optionally also one or more of water, ethane, carbon monoxide, carbon dioxide and/or nitrogen with a molecular oxygen-containing gas in the presence of a catalyst active for the production of vinyl acetate to produce a second product stream comprising vinyl acetate, water, acetic acid and optionally ethylene.

Preferably the integrated process comprises the further steps of:

(c) separating the product stream from step (b) by distillation into an overhead azeotrope fraction comprising vinyl acetate and water and a base fraction comprising acetic acid; and

(d) either (i) recovering acetic acid from the base fraction separated in step (c) and optionally recycling the azeotrope fraction separated in step (c) after partial or complete separation of the water therefrom to step (c),

or (ii) recovering vinyl acetate from the azeotrope fraction separated in step (c) and optionally recycling the base fraction separated in step (c) to step (b),

or (iii) recovering acetic acid from the base fraction separated in step (c)

and recovering vinyl acetate from the overhead azeotrope fraction recovered in step (c).

The catalyst and processes of the present invention will now be further illustrated by reference to the following Examples.

CATALYST PREPARATION

In the following examples and comparative examples, the nominal compositions of the catalysts are given. These were calculated from the amounts of reagents used in the preparations of the catalysts.

Comparative Examples A to G.

The following comparative examples A to G are not examples according to the present invention, because they do not conform to the essential composition of such a catalyst principally in the respect that they do not contain silver and/or iridium. They are included only for the purpose of comparison.

Comparative Example A. ($Mo_{1.00}V_{0.25}Nb_{0.12}O_y$)

A solution *A* was prepared by dissolving 12.71 g ammonium molybdate in 50 ml water heated to 70°C. A second solution *B* was prepared by dissolving 2.11 g ammonium vanadate in 70 ml water heated to 70°C. Another solution *C* was prepared by dissolving 2.43 g niobium chloride and 2.02 g oxalic acid in 50 ml water heated to 70°C. Next, solution *C* was added to solution *B* and the resulting mixture heated at 70°C for 15 minutes. Solution *A* was then added and the final mixture heated at 70°C for 15 minutes, before evaporating the mixture to dryness over not more than 2 hours. The resulting catalyst cake was ground then calcined in static air in an oven at 350°C for 5 hours. The nominal composition of the catalyst was thus $Mo_{1.00}V_{0.25}Nb_{0.12}O_y$.

Comparative Example B($Mo_{1.00}V_{0.25}O_y$)

As for comparative example A except that no solution C was prepared. The nominal composition of the catalyst was thus $Mo_{1.00}V_{0.25}O_y$.

Comparative Example C ($Mo_{1.00}V_{0.25}Nb_{0.12}Pd_{0.01}O_y$)

As for comparative example A except that 0.23 g Pd acetate was added in the preparation of solution A. The nominal composition of the catalyst was thus $Mo_{1.00}V_{0.25}Nb_{0.12}\ Pd_{0.01}O_y$.

Comparative Example D ($Mo_{1.00}V_{0.25}Nb_{0.12}Ru_{0.01}O_y$)

As for comparative example A except that 0.36 g of ammonium Ru hexachloride was added in the preparation of solution A. The nominal composition of the catalyst was thus $Mo_{1.00}V_{0.25}Nb_{0.12}Ru_{0.01}O_y$.

Comparative Example E ($Mo_{1.00}V_{0.25}Nb_{0.12}Rh_{0.01}O_y$)

As for comparative example A except that 0.15 g of Rh (III) hydroxide was added in the preparation of solution A. The nominal composition of the catalyst was thus $Mo_{1.00}V_{0.25}Nb_{0.12}Rh_{0.01}O_y$.

Comparative Example F ($Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ O_y)

Solution A was prepared by dissolving 9.53 g ammonium molybdate and 10.06 g ammonium rhenate in 50 ml water heated to 70°C. Solution B was prepared by dissolving 4.56 g ammonium vanadate in 70 ml water heated to 70°C. Solution C was prepared by dissolving 3.65 g niobium chloride, 1.34 g antimony acetate, 0.26 g calcium nitrate and 4.05 g oxalic acid in 50 ml water heated to 70°C. The rest of the procedure was as in comparative example A. The nominal composition of the catalyst was thus $Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ O_y.

Comparative Example G ($Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ $Pd_{0.011}O_y$).

Solution A was prepared by dissolving 4.76 g ammonium molybdate, 5.03 g ammonium rhenate and 0.06 g palladium acetate in 50 ml water heated to 70°C. Solution B was prepared by dissolving 2.28 g ammonium vanadate in 70 ml water heated to 70°C. Solution C was prepared by dissolving 1.82 g niobium chloride, 0.67 g antimony acetate, 0.26 g calcium nitrate and 1.97 g oxalic acid in 50 ml water heated to 70°C. The rest of the procedure was as in comparative example A. The nominal composition of the catalyst was thus $Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ $Pd_{0.011}O_y$.

Examples according to the present invention

Example I ($Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ $Ag_{0.028}O_y$)

Solution A was prepared by dissolving 6.50 g ammonium molybdate, 6.61 g ammonium rhenate and 0.17 g silver acetate in 50 ml water heated to 70°C. Solution B was prepared by dissolving 3.01 g ammonium vanadate in 70 ml water heated to 70°C. Solution C was prepared by dissolving 1.89 g niobium chloride, 0.88 g antimony acetate, 0.32 g calcium nitrate and 2.24 g oxalic acid in 50 ml water heated to 70°C. The rest of the procedure was as in comparative example A. The nominal composition of the catalyst was thus $Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ $Ag_{0.028}O_y$).

Example II ($Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$ $Ir_{0.028}O_y$)

Solution A was prepared by dissolving 6.50 g ammonium molybdate, 6.61 g ammonium rhenate and 0.49 g ammonium iridium hexachloride in 50 ml water heated to 70°C. Solution B was prepared by dissolving 3.01 g ammonium vanadate

in 70 ml water heated to 70°C. Solution C was prepared by dissolving 1.89 g niobium chloride, 0.88 g antimony acetate, 0.32 g calcium nitrate and 2.24 g oxalic acid in 50 ml water heated to 70°C. The rest of the procedure was as in comparative example A. The nominal composition of the catalyst was thus $Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}Ir_{0.028}O_y$.

Example III ($Mo_{1.00}V_{0.25}Nb_{0.12}Ag_{0.014}O_y$.)

As for example A except that 0.17 g Ag acetate was added in the preparation of solution A. The nominal composition of the catalyst was thus $Mo_{1.00}V_{0.25}Nb_{0.12}Ag_{0.014}O_y$.

Example IV ($Mo_{1.00}V_{0.25}Nb_{0.12}Ag_{0.000028}Ir_{0.0000018}O_y$.)

As for example A. Subsequent analysis revealed the presence of amounts of silver and iridium equivalent to 0.00036 g Ag acetate and 0.0000013 g ammonium Ir chloride in the preparation. The composition of the catalyst was thus $Mo_{1.00}V_{0.25}Nb_{0.12}Ag_{0.000028}Ir_{0.0000018}O_y$.

CATALYST TEST PROCEDURE

Typically 5 mls of catalyst were loaded into a fixed bed reactor made of Hasetelloy grade C276 of dimensions 12mm internal diameter and length 40 cm. Glass beads were used to maintain the catalyst in position in the centre of the reactor. Above the catalyst the glass beads thus acted as a mixing and pre-heating zone for gaseous and liquid reagents. The test apparatus was then pressure-tested at 21 bar with helium to check for leaks. Catalysts were then activated by heating to 220°C at 5°C/min in helium at 21 bar for 16 hours, to ensure full decomposition of catalyst precursors.

The required flows of ethane, 20% oxygen in helium and water were then introduced to the reactor, to ensure an inlet composition of 42% v/v ethane, 6.6% v/v oxygen, 25% v/v helium and 26.4% v/v water (as steam). The total feed flow rate was maintained at a level to ensure a feed GHSV of 2970/h. After equilibrating for 30 minutes, gas samples were taken from the outlet stream to calibrate a GC (model Unicam 4400) for ethane, oxygen and helium. Next, the setpoint temperature of the reactor was increased until typically 75% oxygen conversion was achieved, as indicated by the presence in the outlet stream of 2.2% v/v oxygen.

Following an equilibration period of 30 minutes, catalysts were then evaluated under steady state conditions for a period of typically 4-5 hours. Exit gas volume was measured over the run period by a water-gas meter. Liquid

products were collected and weighed after the run period. Composition of gas and liquid products was measured using GC analysis (Unicam 4400 and 4200 fitted with TCD and FID detectors respectively).

All feed and product flow rates and compositions were entered into an Excel spreadsheet, and the following parameters calculated:

ethane conversion (cnv) = (inlet mol ethane - outlet mol ethane)/inlet mol ethane x100

oxygen conversion (cnv) = (inlet mol oxygen - outlet mol oxygen)/inlet mol oxygen x100

selectivity to AcOH (C-mol %) = (outlet mol AcOH x2)/(mol ethane converted x2) x100

selectivity to ethylene (C-mol %) = (outlet mol ethylene x2)/(mol ethane converted x2) x100

selectivity to CO(C-mol %) = (outlet mol CO)/(mol ethane converted x2) x100

selectivity to CO_2 (C-mol %) = (outlet mol CO_2)/(mol ethane converted x2) x100

selectivity to CO_x (C-mol %) = selectivity to CO + selectivity to CO_2

STY (space time yield) % = (g AcOH)/litre catalyst bed/hour

Typically, mass balance and carbon balance for a reaction was found to be 100 +/- 5%.

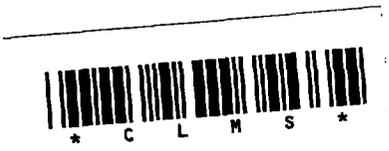
Catalyst comparisons

The following table compares the catalyst performance of the above-described catalysts. Each catalyst was evaluated under standard conditions indicated in the table, except for the temperature, which was varied so as to achieve 70-90 % oxygen conversion, in order to facilitate comparison.

The data in the table illustrates clearly the promotional effect of Ag, Ir and Ag-Ir on Mo-V-Nb based oxide catalysts. Thus, the data in the table clearly illustrate that Ag-promoted catalyst (catalyst I) performs better than unpromoted catalyst (F) in terms of high acetic acid selectivity and low carbon oxides selectivity. In addition, the data indicate that Ir-promoted catalyst (II) is superior to unpromoted catalyst (catalyst F) in terms of higher acetic acid selectivity.

On the basis of these results, Ag and Ir are also both effective catalyst promoters for ethane oxidation to acetic acid in the absence of a Pd promoter.

Example/ Comparative Example	Catalyst Composition	Tset °C	Tbed °C	Ethane cnv %	Oxygen cnv %	$S(C_2H_4)$ % C-mol	$S(CO_x)$ % C-mol	S(AcOH) % C-mol	STY AcOH g/l-cat/h
A	$Mo_{1.00}V_{0.25}Nb_{0.12}$		326	3.2	82.4	41.9	16.2	41.3	82.0
B	$Mo_{1.00}V_{0.25}$		314	4.8	79.4	15.1	67.0	17.8	19.7
C	$Mo_{1.00}V_{0.25}Nb_{0.12}Pd_{0.014}$		253	3.9	76.8	0.0	36.9	62.9	82.4
D	$Mo_{1.00}V_{0.25}Nb_{0.12}Ru_{0.014}$		293	5.0	71.8	43.7	16.5	39.8	70.2
E	$Mo_{1.00}V_{0.25}Nb_{0.12}Rh_{0.014}$		304	5.7	87.5	43.1	15.5	40.3	89.3
F	$Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.03}$	300	309	5.7	75.1	26.3	22.7	50.4	126.0
G	$Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.04}Pd_{0.011}$		286	6.2	73.0	14.8	8.2	76.5	187.8
I	$Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.04}Ag_{0.028}$	250	262	5.7	75.0	19.3	3.6	76.2	183.3
II	$Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.04}Ir_{0.028}$	230	243	2.6	57.2	33.9	3.0	63.0	81.9
II	$Mo_{1.00}Re_{0.69}V_{0.72}Nb_{0.25}Sb_{0.08}Ca_{0.04}Ir_{0.028}$	280	308	5.3	98.8	20.1	20.8	59.1	131.9
III	$Mo_{1.00}V_{0.25}Nb_{0.12}Sb_{0.08}Ag_{0.014}$	280	296	3.4	74.9	33.9	7.2	59.0	100.0
IV	$Mo_{1.00}V_{0.25}Nb_{0.12}Ag_{0.000028}Ir_{0.0000018}$		296	4.1	77.1	28.2	6.8	65.1	124.9
Conditions: 21 bar, 42% v/v ethane, 6.6 % oxygen, 25% water, GHSV = 2970									



Claims:

1. A catalyst composition for the selective oxidation of ethane and/or ethylene to acetic acid which composition comprises in combination with oxygen the elements:-

$$Mo_a.W_b.Ag_c.Ir_d.X_e.Y_f \qquad (I)$$

wherein X is the elements Nb and V;

Y is one or more elements selected from the group consisting of:

Cr, Mn, Ta, Ti, B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Cu, Au, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl, U, Re and Pd;

a, b, c, d, e and f represent the gram atom ratios of the elements such that

$0 < a \leq 1$, $0 \leq b < 1$ and $a + b = 1$;

$0 < (c + d) \leq 0.1$;

$0 < e \leq 2$; and

$0 \leq f \leq 2$.

2. A catalyst composition as claimed in claim 1 in which c and d are such that c + d is at least 10^{-6}.

3. A catalyst composition as claimed in claim 1 or claim 2 in which c and d are such that $(c + d) \leq 0.05$.

4. A catalyst composition as claimed in any one of the preceding claims in which more silver is present than iridium on a gram atom basis.

5. A catalyst composition as claimed in claim 4 in which c is at least 10 times d.

6. A catalyst composition as claimed in any one of the preceding claims in which e is at least 0.05, preferably at least 0.2.

7. A catalyst composition as claimed in any one of the preceding claims in which e is no greater than 0.5.

* C L M S *

8. A catalyst composition as claimed in any one of the preceding claims in which f is at least 10^{-6}.

9. A catalyst composition as claimed in any one of the preceding claims in which f is no greater than 0.2.

10. A catalyst composition as claimed in any one of the proceedings claims in which Y is at least one element selected from the group consisting of Cu, Pd, Pt, Re, Ru and Sb.

11. A catalyst composition as claimed in any one of the preceding claims in which a is at least 0.1, preferably at least 0.5.

12. A catalyst as claimed in any one of the preceding claims in which b is no greater than 0.9.

13. A catalyst composition selected from the group consisting of :

$Mo_a.W_b.Ag_c.X_e\ Y_f$; $Mo_a.W_b.Ir_d.X_e\ Y_f$; $Mo_a.W_b.[Ag+Ir]_{c+d}.X_e.Y_f$;

$Mo_a.Ag_c.X_e.Y_f$; $Mo_a.Ir_d.X_e.Y_f$; $Mo_a.[Ag+Ir]_{c+d}.X_e.Y_f$; $[Mo+W]_{a+b}.Ag_c.X_e.Y_f$;

$[Mo+W]_{a+b}.Ir_d.X_e.Y_f$; $[Mo+W]_{a+b}.[Ag+Ir]_{c+d}.X_e.Y_f$

wherein a, b, c, d, e, and f are as defined in any one of the preceding claims;

$Mo_{1.00}.Re_{0.69}.V_{0.72}.Nb_{0.25}.Sb_{0.08}.Ca_{0.03}.Ag_{0.028}Oy$;

$Mo_{1.00}.Re_{0.69}.V_{0.72}.Nb_{0.25}.Sb_{0.08}.Ca_{0.03}.Ir_{0.028}Oy$;

$Mo_{1.00}.V_{0.25}.Nb_{0.12}.Ag_{0.014}Oy$; and

$Mo_{1.00}.V_{0.25}.Nb_{0.12}.Ag_{0.000028}.Ir_{0.0000018}Oy$

wherein y is a number which satisfies the valencies of the elements in the composition for oxygen.

14. A process for the production of acetic acid from a gaseous mixture comprising ethane and/or ethylene which process comprises contacting the gaseous mixture with a molecular oxygen-containing gas at elevated temperature in the presence of a catalyst composition as claimed in any one of claims 1 to 13.

15. The use of a catalyst composition as claimed in any one of claims 1 to 13 in an integrated process for the production of acetic acid and/or vinyl acetate which comprises the steps :

(a) contacting in a first reaction zone a gaseous feedstock comprising ethylene and/or ethane and optionally steam with a molecular oxygen-containing gas in the presence of a catalyst active for the oxidation of ethylene to acetic acid and/or ethane to acetic acid and ethylene as claimed in any one of claims 1 to 13, to produce a first product stream comprising acetic acid, water and ethylene (either as unreacted ethylene and/or as co-produced

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ethylene) and optionally also ethane, carbon monoxide, carbon dioxide and/or nitrogen; and

(b) contacting in a second reaction zone in the presence or absence of additional ethylene and/or acetic acid at least a portion of the first gaseous product stream comprising at least acetic acid and ethylene and optionally also one or more of water, ethane, carbon monoxide, carbon dioxide and/or nitrogen with a molecular oxygen-containing gas in the presence of a catalyst active for the production of vinyl acetate to produce a second product stream comprising vinyl acetate, water, acetic acid and optionally ethylene.

16. The use as claimed in claim 15 of a catalyst composition as claimed in any one of claims 1 to 13 in an integrated process for the production of acetic acid and/or vinyl acetate which comprises the further steps of:

(c) separating the product stream from step (b) by distillation into an overhead azeotrope fraction comprising vinyl acetate and water and a base fraction comprising acetic acid;

(d) either (i) recovering acetic acid from the base fraction separated in step (c) and optionally recycling the azeotrope fraction separated in step (c) after partial or complete separation of the water therefrom to step (c),

or (ii) recovering vinyl acetate from the azeotrope fraction separated in step (c) and optionally recycling the base fraction separated in step (c) to step (b),

or (iii) recovering acetic acid from the base fraction separated in step (c) and recovering vinyl acetate from the overhead azeotrope fraction recovered in step (c).